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THE EFFECT OF ADDITIVES ON LITHIUM
CYCLING IN PROPYLENE CARBONATE

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20. Abstract (Cont.)

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A mechanism of loss of efficiency during lithium cycling and also on open circuit stand has been formulated: Granules of lithium are encapsulated by an insulating film of propylene carbonate-lithium reaction products, thus severing electrical contact with the substrate. The additives have been postulated to form Li^+ -conductive films on the deposit, allowing the deposition onto the granules and their growth into larger granules, and retarding insulation. On open circuit stand, the long-term equilibrium favors the formation of an insoluble insulating (Li-PC) film over the partially soluble, Li^+ -conductive film. It is suggested that such behavior limits the usefulness of propylene carbonate in secondary lithium batteries.

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THE EFFECT OF ADDITIVES ON LITHIUM CYCLING IN PROPYLENE CARBONATE

ABSTRACT

Deposition and discharge of lithium on an inert (nickel) substrate in 1M LiClO₄/propylene carbonate (PC) has been studied as a function of plating and stripping currents, cycle number, and electrolyte composition. Water (<1200 ppm), nitromethane, and SO₂ were found to enhance the cycling efficiency, which was relatively low in the dry electrolyte without additives. In all cases, marked deterioration in efficiency was noted after 10 to 20 repeated cycles. Electrodeposited lithium was found to corrode initially (over the first 10,000 seconds of its life) at an average rate of 30-40 $\mu\text{A}/\text{cm}^2$, independent of the additive within experimental error. The corrosion rate of the deposit decreases with time, and reaches a limiting value of 5-10 $\mu\text{A}/\text{cm}^2$. This rate is also not improved by presence of additives.

A mechanism of loss of efficiency during lithium cycling and also on open circuit stand has been formulated: Granules of lithium are encapsulated by an insulating film of propylene carbonate-lithium reaction products, thus severing electrical contact with the substrate. The additives have been postulated to form Li⁺-conductive films on the deposit, allowing the deposition onto the granules and their growth into larger granules, and retarding insulation. On open circuit stand, the long-term equilibrium favors the formation of an insoluble insulating (Li-PC) film over the partially soluble, Li⁺-conductive film. It is suggested that such behavior limits the usefulness of propylene carbonate in secondary lithium batteries.

INTRODUCTION

The efficient electroplating and stripping of lithium in non-aqueous media is essential to the development of ambient temperature, secondary lithium batteries. Lithium has been reported "stable" in a number of solvents, although the criterion for stability has often been the failure to observe visually reaction between bulk lithium and the hot liquid (1). One of the most common media for use in lithium batteries has been propylene carbonate (PC). Yet, recent evidence exists both for the non-Nernstian behavior of the Li (Hg)/Li⁺ (PC) couple (2), and for the corrosion of electroplated lithium in PC (3). These results are actually in accordance with the earlier work of Butler, Cogley and Synnott (4) in which filming was observed through a gradual lowering of the exchange current of freshly cut

lithium in contact with PC. Such films can protect bulk lithium from further solvent decomposition, thus explaining the discrepancy between results obtained for bulk lithium and for high surface area electroplated lithium or for lithium amalgam.

Theoretically, at least, the problem of corrosion of electroplated lithium can be alleviated by controlling the filming observed by Butler et al. so that the deposited lithium becomes passivated. Such passivation is readily observed, though not thoroughly understood, for bulk lithium in SOCl_2 (5,6,7) or in SO_2 plus numerous diluents (8). A further advantage for the use of this phenomenon in batteries is that the films, though impermeable to corrosive solvents and depolarizers, are conductive to Li^+ . Thus, they allow discharge of primary cells based upon Li/SOCl_2 , and presumably discharge and recharge in SO_2 /nonaqueous solvent systems (8).

If the passivation of lithium following electrodeposition from a nonaqueous electrolyte can be achieved, secondary lithium batteries containing soluble cathode materials, with their implications of high discharge rates, may be considered. In such a system, a film-forming material (the "precursor"), such as SO_2 , would be introduced. This precursor would form a thin film on the lithium, protecting the metal from further attack, while still allowing its plating and discharge. Hence, it is important to assess the effect of possible precursors on the properties of electrodeposited lithium.

The purpose of the present study is to observe the effects of three additives on the cycling efficiency, cycle life and corrosion of lithium in PC: SO_2 , nitromethane (NM), and H_2O . SO_2 and H_2O are known to have the capability of forming passivating films on lithium. NM has been used as an additive to PC in lithium batteries (9), apparently to facilitate mass transport, and its effect upon corrosion and efficiency is assessed here primarily to determine its practical usefulness as an additive to secondary cells.

EXPERIMENTAL

1. Solvents and Solutions. PC (Matheson, Coleman and Bell, Reagent Grade), was light yellow in color, as received. Karl Fischer analysis showed less than 30 ppm H_2O in a freshly opened bottle, although PC did tend to pick up water from the atmosphere if not tightly sealed. Distillation was carried out in a Perkin-Elmer 251 spinning band column at 1 mm pressure and a 2:1 reflux ratio. The colorless middle 60% fraction was collected at 60°C . After back-filling with argon, the receiver was transferred to a dry atmosphere argon-filled glove box (Vacuum-Atmospheres).

Solutions were prepared 1M in either LiAlCl_4 (Foote Mineral Company) or, more often, LiClO_4 (Alfa, anhydrous). It was necessary

to add the LiAlCl_4 slowly to avoid a high heat of solution and a yellowing of the solvent. This yellowing was more easily avoided if the salt were added to PC containing lithium dispersion. Anhydrous LiClO_4 was determined by Karl Fischer analysis to contain 1.5% H_2O by weight. In order to reduce the H_2O content of such solutions below the Karl Fischer detection limit of about 10 ppm, the solutions were dried for three, 24 hour periods with fresh portions of Linde 5A, 600 mesh molecular sieve (Alfa) which had been activated for 12 hours at 400°C , and subsequently stored in a vacuum.

Stock solutions containing SO_2 (Matheson, anhydrous) were prepared by directly bubbling the gas into the solvent. The SO_2 concentration was determined by weight. The solutions were then dried over activated molecular Linde 3A, 600 mesh sieve.

PC/ SO_2 solutions which had been allowed to stand in the dry box over molecular sieves for at least five days assumed a golden color. If the SO_2 were allowed to evaporate, the color disappeared. Because the origin of this effect is unknown, solutions of SO_2 in PC were used soon after preparation. NM (Matheson, Coleman, Bell, spectro-quality) was treated with lithium dispersion before use.

2. Cell Design and Construction. The cell used most frequently in the lithium deposition and stripping studies is illustrated in Fig. 1. The working electrode was constructed from 0.5 inch wide 5 mil nickel ribbon to which a nickel lead had been soldered at one end, not in contact with the solution. The plating area, first cleansed by sanding and rinsing with methanol, was masked off with Teflon. One convenient method for doing this was to mask with Teflon tape, then to press the electrode at 5,000 psi, thus bonding the Teflon to the substrate. The counter electrode was made from 2" x .015" lithium metal ribbon (Foote Mineral Company) pressed onto expanded nickel screen at 1,000 psi. The reference capillary was constructed from a pasteur pipette whose tip was packed with pieces of prebaked fiberglass paper. The vial had a polyethylene cap which snapped over the electrode leads, and which had a hole in the center to hold the reference electrode compartment. The latter contained lithium and a 1M solution of Li^+ in PC.

Another type of cell, illustrated in Fig. 2, was used for viewing lithium deposition with a microscope. The working electrode was a 1/4 inch diameter nickel rod (Research Organic/Research Inorganic Chemical Corp., 99.9%) encased in Teflon, except for the end which comprised the plating surface. The counter electrode was a lithium ring, situated at the bottom of the cell. As the cell had to be used outside the glove box, leads to the outside were made air tight using Teflon adaptors and Teflon tape.

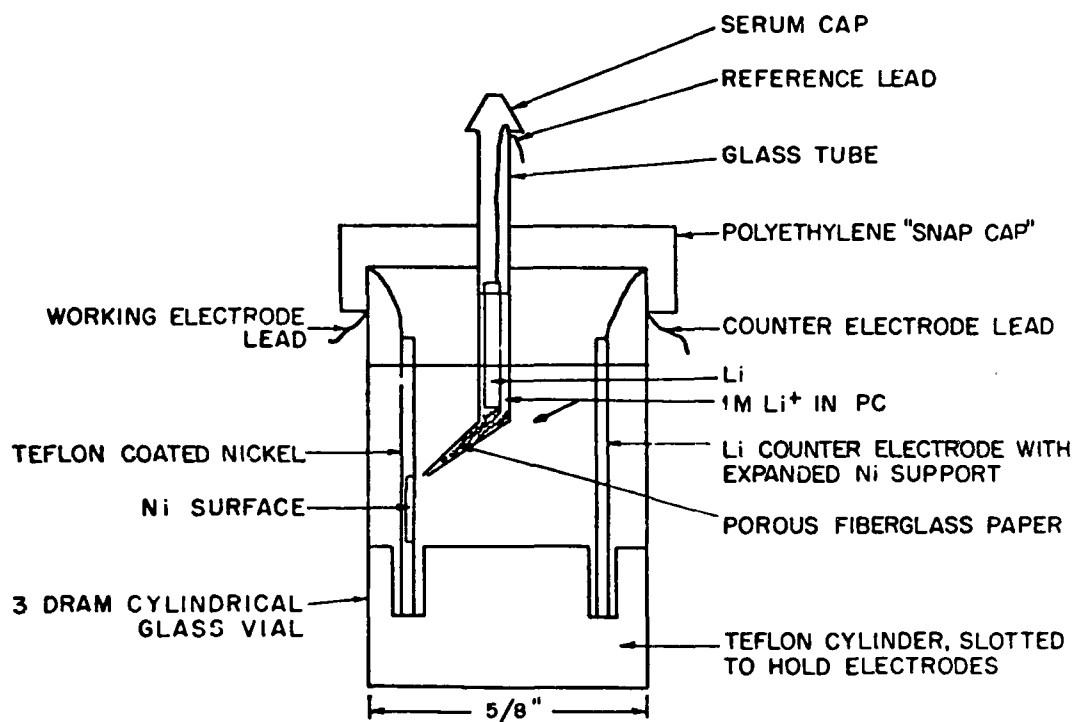


Fig. 1: Cell for lithium cycling experiments.

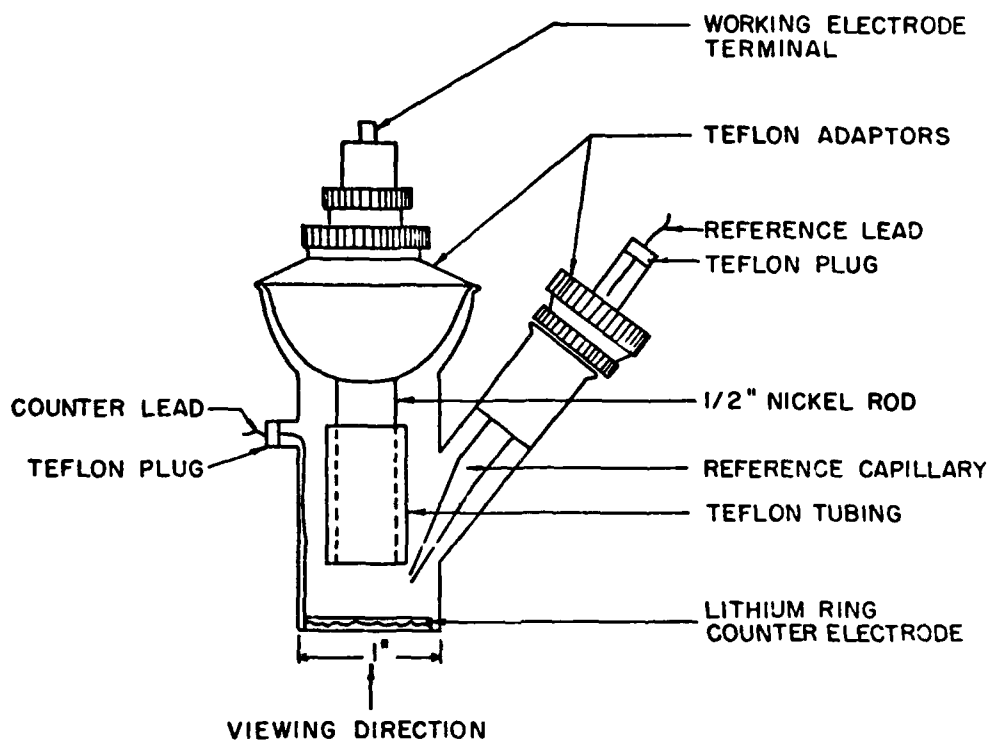


Fig. 2: Cell for viewing lithium deposition.

3. Electrochemical Measurements. Lithium plating and stripping were carried out galvanostatically using a Princeton Applied Research Model 373 potentiostat-galvanostat. The potential between the working and reference electrodes (1M Li/Li⁺) was monitored on an EAI 1130 X-Y recorder. The potential time profile for cyclic voltammetry was generated using a Wavetek Model 133 low frequency trigger generator. All potentials are reported vs. 1M Li/Li⁺.

RESULTS

1. The Lithium Electrode - Efficiency Measurements. A few studies have appeared in the literature concerning the efficiency of plating and stripping lithium in nonaqueous solutions of Li⁺ salts (3,10-15). As is evident from Table 1, reports of the efficiency of the lithium plating-stripping cycle at room temperature in PC vary considerably. It appears that the overall efficiency may be a function of a number of parameters, especially solvent, solvent polarity, supporting electrolyte, substrate, plating charge, plating and stripping current densities, and electrode orientation. Because the overall efficiency of lithium cycling is a multi-determined variable, the results of past studies cannot be comparatively interpreted. The one thing that is clear is that there are substantial difficulties in cycling lithium efficiently.

In the present work, lithium was plated (p) and stripped (s) galvanostatically. The overall efficiency of the process is

$$\text{Eff} = \frac{i_s t_s}{i_p t_p} = \frac{Q_s}{Q_p} \quad [1]$$

The open circuit potential of the nickel electrode versus the Li/Li⁺ reference was independent of solvent. In PC, methyl acetate, methyl chloroformate and DMSO, the OCP was +2.4V. The potential-determining reaction was not elucidated.

When the current was turned on, the potential of the electrode fell immediately to a cathodic maximum overshoot, then rose within a few seconds to a cathodic plateau. In a cell like that in Fig. 1, the overshoot was typically 500 mV and the plateau was 200 mV, at 5 mA/cm², uncorrected for iR (25-50Ω). Reversing the current to strip the deposit, no overshoot was noted, even after waiting several hours after plating. The plateau stripping (anodic) potential was approximately equal to the plateau plating (cathodic) potential, although a tendency toward higher potentials was often noted as a function of stripping time. At the stripping end point, the potential increased very rapidly. A cutoff potential of +1.0V was assumed for efficiency calculations. The current was turned off at this point to avoid any chance of dissolution of the nickel substrate. An example of a plating-stripping chronopotentiogram is shown in Fig. 3.

Table 1: Efficiencies of Cycling Lithium in Solutions of PC-Li Salts,
as Reported in the Literature

Electrolyte	Substrate	Q (coul/cm ²)	i_{plate} (mA/cm ²)	i_{strip} (mA/cm ²)	Efficiency	Comments	Ref.
0.75M AlCl ₃ , Sat. LiCl	Ni	0.18	10	10	78%	Up-facing Ni Electrode	10
		1.8	10	10	89%		
		18.0	10	10	72%		
1M LiClO ₄	Mg	1.8	10	10	43%	Down-facing Ni Electrode	10
		1.16	53	0.2	67%	Recovery from "fresh" alloying substrate.	11
1M LiAlCl ₄	Ag	0.9	1	1	60% (max)	Efficiency varies with cycle. Alloying sub- strate.	12
LiBF ₄ or LiAlCl ₄	Be	-	1	1	95%	From an abstract.	13
	Cu	-	1	1	40%		
1M LiAlCl ₄	Ni	0.1-1.0	0.5-6.0	0.5-6.0	25-70%	Q varied with $i_p (=i_s)$	16
1M LiClO ₄	Brass	4.5-18.0	2.5	2.5	60%		3

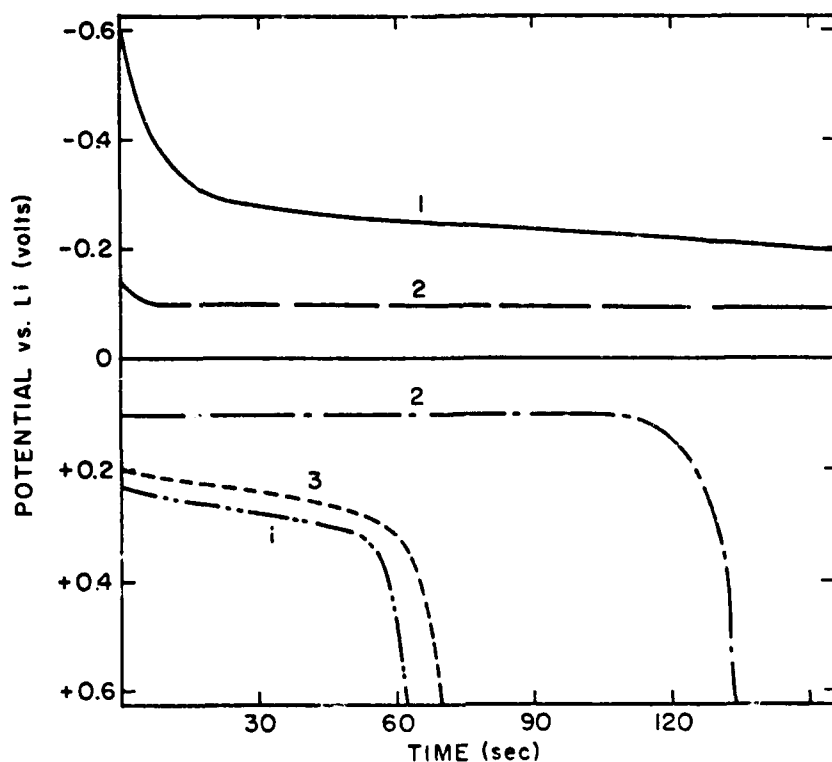


Fig. 3: Lithium plating and stripping chronopotentiograms, on a nickel substrate, in propylene carbonate, 1M LiAlCl₄. Plating current (i_p) = 3 mA/cm² = stripping current (i_s).

1. No additives; Efficiency = 40% after 20 cycles.
2. 1% SO₂ added to cell immediately after stripping of 1. After five minutes, plating curve 2 was recorded, followed by immediate stripping. Efficiency = 84%.
3. 1% SO₂ added; deposit stripped after 1.5 hours; Efficiency = 45%.

Lithium was first plated and stripped from 1M Li^+/PC solutions containing less than 10 ppm H_2O , and the efficiency was observed as a function of plating and stripping current density and cycle number. The charge was held constant.

Efficiencies in these dry solutions were generally quite low, 38 to 50%, depending on plating and stripping current density, for a charge of 1 coul/cm². As noted previously by Selim and Bro (3), lithium remains on the working electrode after the electrochemical end point has been reached. This phenomenon was observed under 50X and 100X magnification.

A special cell (Fig. 2) was constructed for viewing lithium deposition on a nickel surface using a Unitron Series N Metallograph. Lithium was first plated at 1 mA/cm² for a 1M LiAlCl_4 solution. The deposit appeared dull brown to gray, and was homogeneously distributed on the electrode surface. The deposit was then removed galvanostatically. After the dissolution was apparently complete electrochemically, it was obvious that an even coating of lithium remained on the nickel surface. Repeated plating and stripping gave rise to pitted areas on the lithium surface. With each cycle, the deposit became more dendritic, with many areas of very loose deposits. Dendrites were also formed more readily at higher plating and stripping currents. In addition, the dendrites were difficult or impossible to remove electrochemically, even using low current densities or potentiostatically.

For these small charges, the efficiency showed a moderate increase with increasing plating current density, up to 20 mA/cm². Except at very low stripping current densities, where the efficiency was adversely affected, the efficiency was relatively insensitive to i_s . These results are summarized in Fig. 4.

Efficiency as a function of cycle number was compared for solutions 1M in LiAlCl_4 and 1M in LiClO_4 ($i_p = i_s = 2.5 \text{ mA/cm}^2$, $Q = 0.5 \text{ coul/cm}^2$). The efficiency over the first few cycles was generally higher for this charge than for 1 coul/cm² reported above. In addition, the Li cycling process was more efficient for LiAlCl_4 than for LiClO_4 -based electrolytes. Both systems showed a decline in efficiency after a few cycles. The results are shown in Fig. 5. Examination of the working electrodes following their effective "failure" revealed a grey lithium slurry on their surfaces, indicating that most plating sites were being blocked by insulated deposits. The efficiency characteristic on the first cycles could be regenerated by wiping clean or replacing the working electrode. Cyclic voltammetry of these "cycled" solutions revealed no new electroactive impurities between +0.8 and +4.5V vs. Li/Li^+ on Pt, and out to 0.0V on nickel.

2. Corrosion of Electrodeposited Lithium. Two methods were used to measure the rate of corrosion of lithium which had been electro-

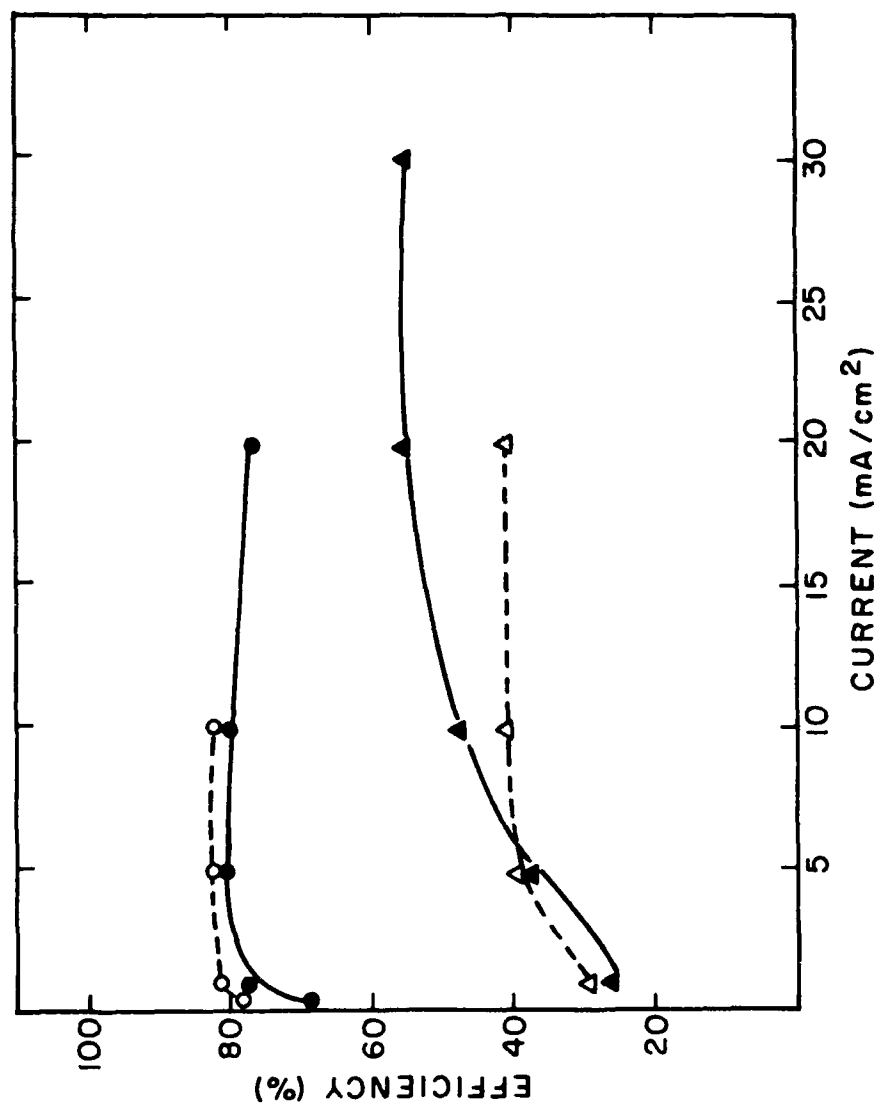


Fig. 4: Coulombic efficiencies of cycling lithium on nickel in propylene carbonate, 1M LiClO₄, as a function of plating and stripping current densities.
 (A) $\bar{i}_s = 5 \text{ mA/cm}^2$, i_p variable; (Δ) $i_p = 5 \text{ mA/cm}^2$, \bar{i}_s variable;
 (●) 15% (vol) nitromethane, $\bar{i}_s = 5 \text{ mA/cm}^2$, i_p variable;
 (○) 15% (vol) nitromethane, $i_p = 5 \text{ mA/cm}^2$, \bar{i}_s variable.

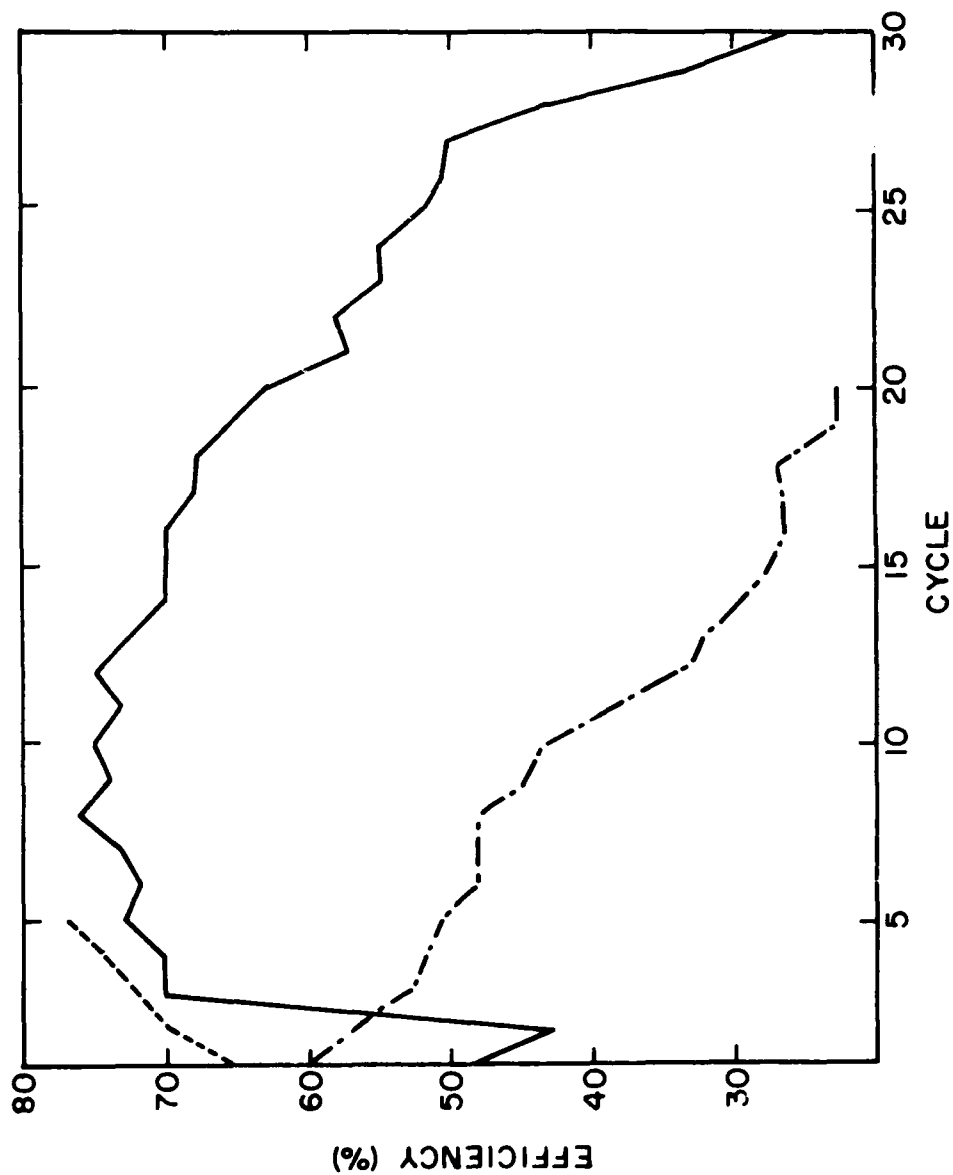


Fig. 5: Effect of repeated cycling on the lithium plating-stripping efficiency in propylene carbonate using a nickel substrate; $i_p = i_s = 2.5 \text{ mA/cm}^2$; coulombs plated (Q_p) = 0.45 coul/cm^2 . (—) 1M LiAlCl_4 ; (---) 1M LiAlCl_4 , beginning with 31st cycle after wiping working electrode; (- - -) 1M LiClO_4 .

deposited onto nickel. In the first, or "standing corrosion" method, a certain charge of lithium was plated onto the nickel, and the open circuit potential of the electrode versus a Li/Li^+ reference was monitored as a function of time. The potential remained at zero until the bare substrate became exposed, at which point the potential rapidly became anodic. The corrosion current was calculated as

$$i_c = \frac{Q_0}{t} \quad [2]$$

where Q_0 is the amount of lithium (per cm^2) which can be removed at $t = 0$ and t is the time, in seconds, for all the plated lithium to corrode away.

The "standing corrosion" experiment yields only an average value of the corrosion current, as i_c can change with time. The time dependence of i_c was measured in the following way. Four cells were plated in series. At varying intervals, the lithium was stripped from one of the working electrodes. The cells were permuted, plated again, and again stripped at the same intervals. This procedure was carried out two or more times, until each cell had been stripped after each of four waiting intervals. The amount of lithium which could be removed was averaged for each waiting time period, and was graphed as a function of time.

Standing corrosion experiments. Data on the corrosion of 1 coul/ cm^2 of lithium plated from PC/1M Li^+ solutions as a function of H_2O concentration and supporting electrolyte are summarized in the last column in Table 2. These data reveal an average corrosion rate (i_c [open circuit]) of electrodeposited lithium in the presence of 1M LiClO_4 in dry PC to be 10-35 $\mu\text{A}/\text{cm}^2$. Values of i_c obtained in this manner were somewhat irreproducible, within these limits. This irreproducibility is probably due to morphology variations resulting from microscopic differences in the substrate surface, plating current density, and a sensitivity of i_c to the presence of certain impurities removable by distillation, but which may reform thermally or via hydrolysis.

Water concentration affected the efficiency of cycling more greatly than the corrosion rate (vide infra). The corrosion rate observed in dry solutions was actually somewhat higher than for solutions containing 1200 ppm H_2O . Going from 10^3 to 10^4 ppm H_2O resulted in a fourfold increase in i_c and a threefold decrease in cycling efficiency.

LiAlCl_4 gave a consistently higher corrosion rate than well-dried solutions of LiClO_4 . It was not determined whether the inferiority of the LiAlCl_4 was due to an impurity in the salt, or to

HCl, an hydrolysis produced of LiAlCl_4 . The salt is prepared using excess LiCl , so attack by lithium by AlCl_3 should be ruled out.

The baseline efficiency of lithium cycling was often lower after a standing corrosion experiment than before. This is probably due to the formation of residual insulating black deposits on the substrate, resulting in an inhomogeneous plating surface.

It should be stressed that lithium ribbon remains shiny and unpitted indefinitely in 1M LiClO_4 or 1M LiAlCl_4 solutions of PC. Only with such "dense" lithium may the formation of surface films passivate against extensive corrosion. The high corrosion rate of electrodeposited lithium is probably due to the diffuse nature of the deposit in this solvent, giving rise to a high surface area. Lithium in this form is highly susceptible to attack by solvent and impurities. Insulating reaction products can also isolate granules of deposit, making them difficult to remove electrochemically.

Corrosion-time experiments. Fig. 6 shows the variation of i_c with time, as measured by the method outlined above. Corrosion of electrodeposited lithium was always highest immediately following plating, and decreased with time. The initial and limiting values of i_c measured by this method are also included in Table 2. Solutions containing LiAlCl_4 were more corrosive than those containing LiClO_4 , verifying the "standing corrosion" results. It should be noted that in none of these experiments was the electroplated lithium found to be completely passivated against attack: All the plated lithium would disappear after enough time.

3. Additive Effects.

H_2O . The efficiency of lithium cycling in 1M LiClO_4 was determined as a function of H_2O concentration. The results are reported in Fig. 7. Solutions containing up to 1,200 ppm H_2O actually show improved lithium cycling efficiency compared to the dry solutions. At higher H_2O concentrations, the efficiency drops and gassing can be detected.

SO_2 . Fig. 3, curve 2, illustrates the potential-time curve for galvanostatic lithium plating and stripping for a cell 1M in LiAlCl_4 which had been cycled 20 times. After curve 1 was reported, enough SO_2 was added to the cell to make its concentration 1% by weight. Curve 2 shows that this increased the cycling efficiency dramatically, from 40 to 84%. Plating and stripping also occurred at a lower potential in the SO_2 containing solutions, reflecting perhaps a higher solution conductivity.

Similar results were obtained for 1M LiClO_4 , 1% SO_2 solutions. Thorough drying was important before the addition of SO_2 , because

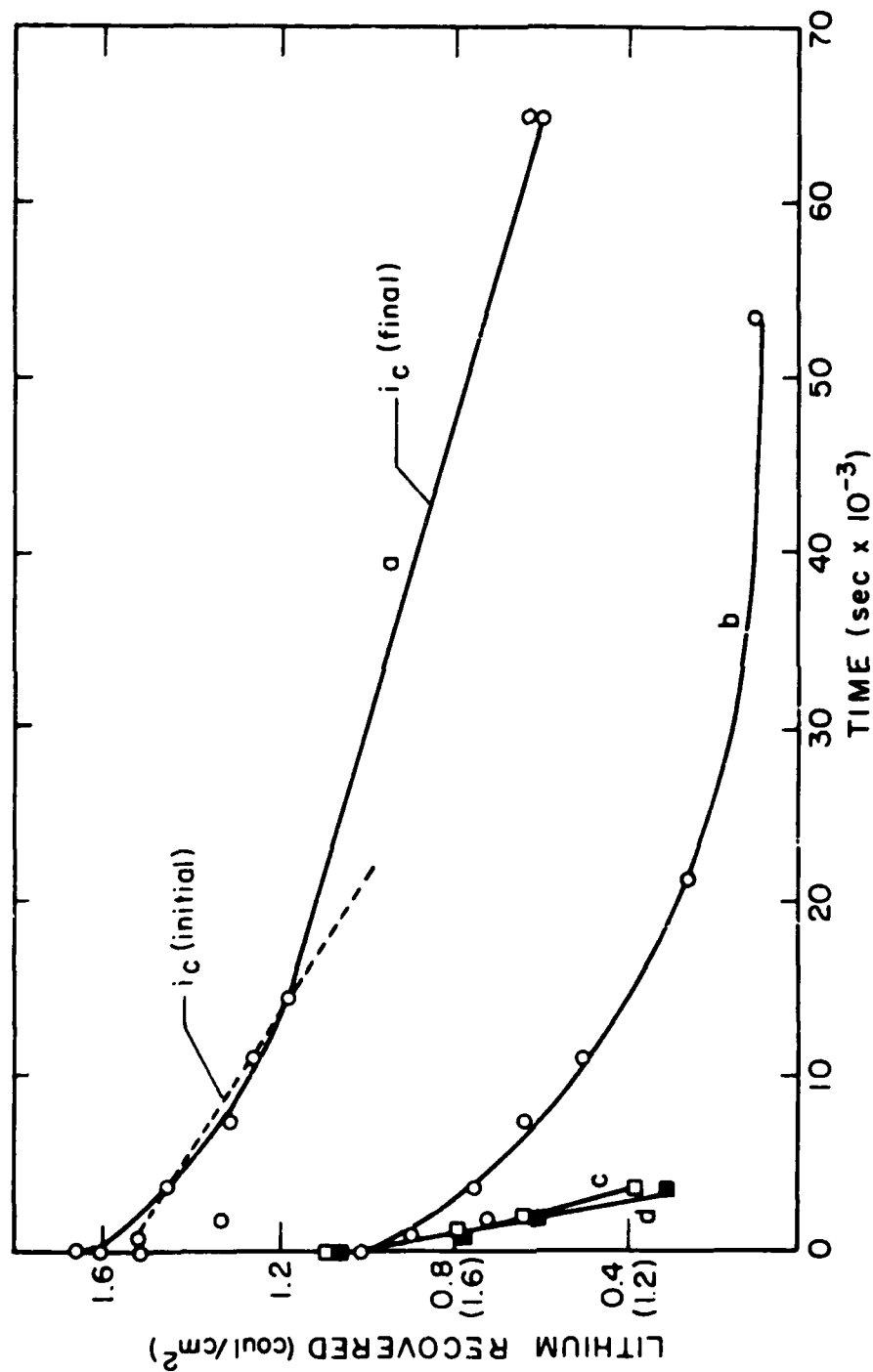


Fig. 6: Corrosion of lithium electrodeposited onto nickel in propylene carbonate; $i_p = i_s = 5 \text{ mA/cm}^2$.
 (a) 1M LiClO₄, 5% (wt) SO₂. $Q_p = 1.75 \text{ coul/cm}^2$, $i_c(\text{initial}) = 25 \text{ } \mu\text{A/cm}^2$, $i_c(\text{final}) = 11 \text{ } \mu\text{A/cm}^2$.
 (b) 1M LiClO₄, $Q_p = 1.75 \text{ coul/cm}^2$, $i_c(\text{initial}) = 43 \text{ } \mu\text{A/cm}^2$, $i_c(\text{final}) = 5 \text{ } \mu\text{A/cm}^2$.
 (c) 1M LiAlCl₄, 5% (wt) SO₂. Q scale in parentheses. $Q_p = 2 \text{ coul/cm}^2$, $i_c = 0.15 \text{ mA/cm}^2$.
 (d) 1M LiAlCl₄, $Q_p = 2 \text{ coul/cm}^2$, $i_c = 0.17 \text{ mA/cm}^2$.

Table 2

Corrosion rates of lithium electrodeposited onto nickel in propylene carbonate.
 $i_c(\text{initial})$ = corrosion rate from 0 to 10,000 sec after plating; $i_c(\text{limiting})$
 = corrosion rate after 20,000 sec; $i_c(\text{open circuit})$ = corrosion rate measured
 by monitoring open circuit potential (see text).

Solution	Q_p ($\mu\text{C}/\text{cm}^2$)	i_p (mA/cm^2)	$i_c(\text{initial})$ ($\mu\text{A}/\text{cm}^2$)	$i_c(\text{limiting})$ ($\mu\text{A}/\text{cm}^2$)	$i_c(\text{open circuit})$ ($\mu\text{A}/\text{cm}^2$)
1M LiAlCl ₄	1.0 2.0	5 5	- 170	- 170	115 -
1M LiClO ₄	1.0 1.0 1.0 1.75	1 5 20 5	- - - 43	- - - 5	35 32 10 -
1M LiClO ₄ 5% (wt) SO ₂	1.75	5	25	11	-
1M LiAlCl ₄ 5% (wt) SO ₂	2.0	5	150	150	-
1M LiClO ₄ , 0.1M NM (untreated)	1.5	5	112	-	-
1M LiClO ₄ , 0.1M NM (treated with lithium)	1.5 1.0	5 10	35 -	- -	- 28
1M LiClO ₄ , 1200 ppm H ₂ O	1.0	5	-	-	20
1M LiClO ₄ , 1200 ppm H ₂ O, undistilled PC	1.0	10	-	-	118
1M LiClO ₄ , 10 ⁴ ppm H ₂ O	1.0	5	-	-	80

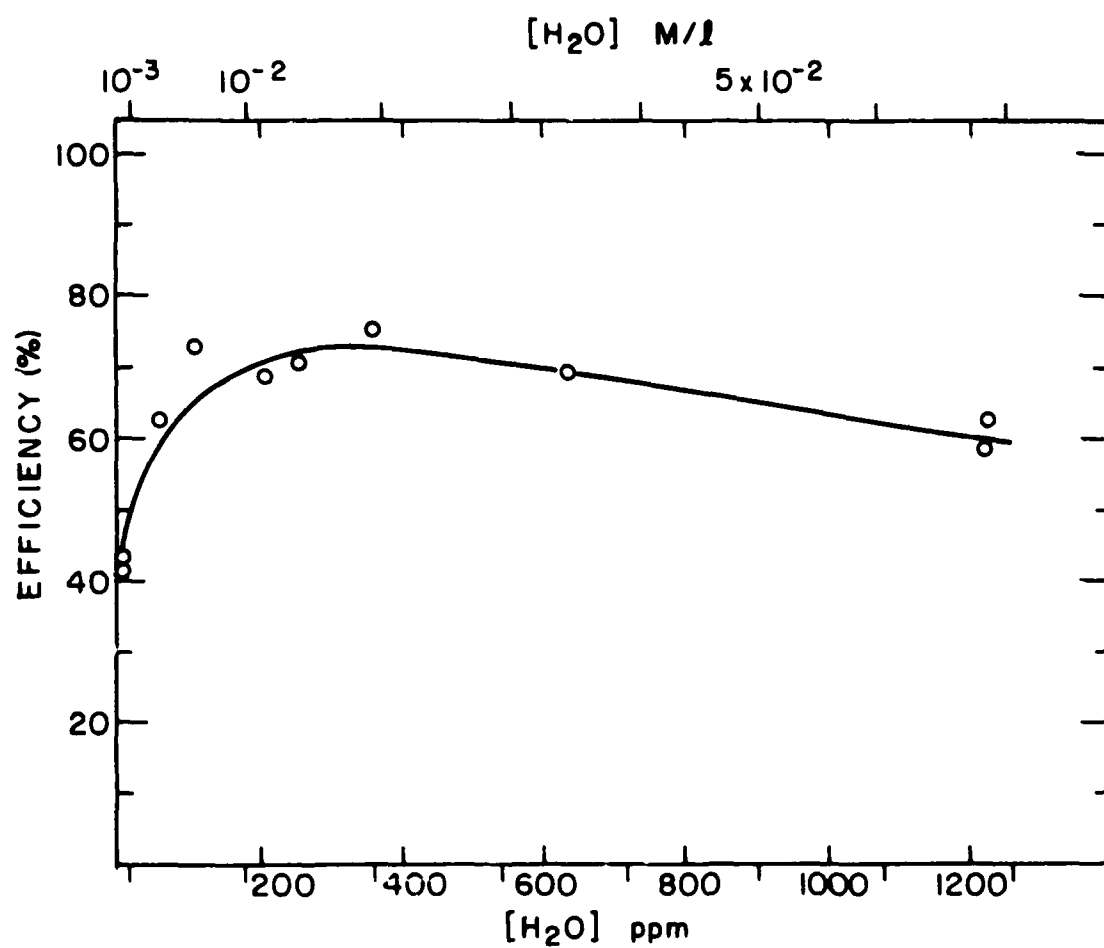


Fig. 7: Effect of H₂O on the efficiency of cycling lithium on nickel in propylene carbonate, 1M LiClO₄; $i_p = i_s = 5 \text{ mA/cm}^2$; $Q_p = 1 \text{ coul/cm}^2$.

residual water would react with SO_2 to yield H_2SO_3 , which would rapidly attack lithium. A solution of sieve-dried PC, 1M "anhydrous" LiClO_4 , and 1% SO_2 (obtained from a sieve-dried 30% SO_2 in propylene carbonate stock solution) gave only 33% lithium cycling efficiency ($Q = 1 \text{ coul/cm}^2$). After drying, the efficiency was increased to 91%.

An experiment to determine the optimum SO_2 concentration was carried out. The results, however, were complicated by variations in the dependence of efficiency versus cycle with SO_2 concentration. In the concentration region of 0.01 to 0.05M SO_2 , results were extremely irreproducible, with efficiencies ranging from 50 to 75% on the first cycle of 1 coul/cm² and dropping to below 50% on subsequent cycles. Above 0.1M SO_2 , the first cycle was consistently above 80%. Thus, no regular curve of efficiency versus SO_2 concentration could be constructed.

The cycling efficiency of PC/ SO_2 solutions was further investigated as a function of cycle number for a constant charge. The efficiency decreased rapidly over the first 5 to 10 cycles, but more rapidly for a charge of 1 coul/cm² than for a charge of 0.33 coul/cm². These results are reported in Fig. 8. The decline in efficiency could be remedied somewhat by waiting between cycles. This effect gave rise to the spiked appearance of the graphs in Fig. 8 at the points where a waiting period between cycles was observed. This spiking effect was not observed for the PC/ H_2O system over the H_2O concentration range studied.

The effect of additive concentration on the cycling efficiency is thus somewhat different for NM, SO_2 and H_2O . The smooth curves of efficiency vs. [NM] (Fig. 9), and the diminished spiking in the efficiency vs. cycle curve (except for the later cycles) (Fig. 10) indicate that NM is not consumed, or consumed very little, during electroplating. The same appears true for H_2O at concentrations below about 1,200 ppm. At higher H_2O concentrations, gassing occurs during plating. Cyclic voltammetry of PC/ LiClO_4 solutions, on platinum or nickel, shows no new peaks between +0.8 and +4.5V vs. Li/Li^+ when NM is added. Water reduction appears at +1.5V vs. Li/Li^+ , but the reduction rate at low concentrations is considerably lower than the diffusion limit (17). Hence, with added H_2O , there is always enough present to interact with the surface of as-plated lithium. Conversely, the spiking observed in the efficiency vs. cycle curve for SO_2 indicates the consumption of SO_2 during plating, and the necessity for waiting between cycles to replenish the SO_2 at the electrode surface. Cyclic voltammetry indicates that SO_2 reduces on platinum at +2.5V vs. Li/Li^+ .

Fig. 6 shows corrosion as a function of time for a total plating charge of 2 coul/cm² in solutions 1M in LiClO_4 with and without SO_2 .

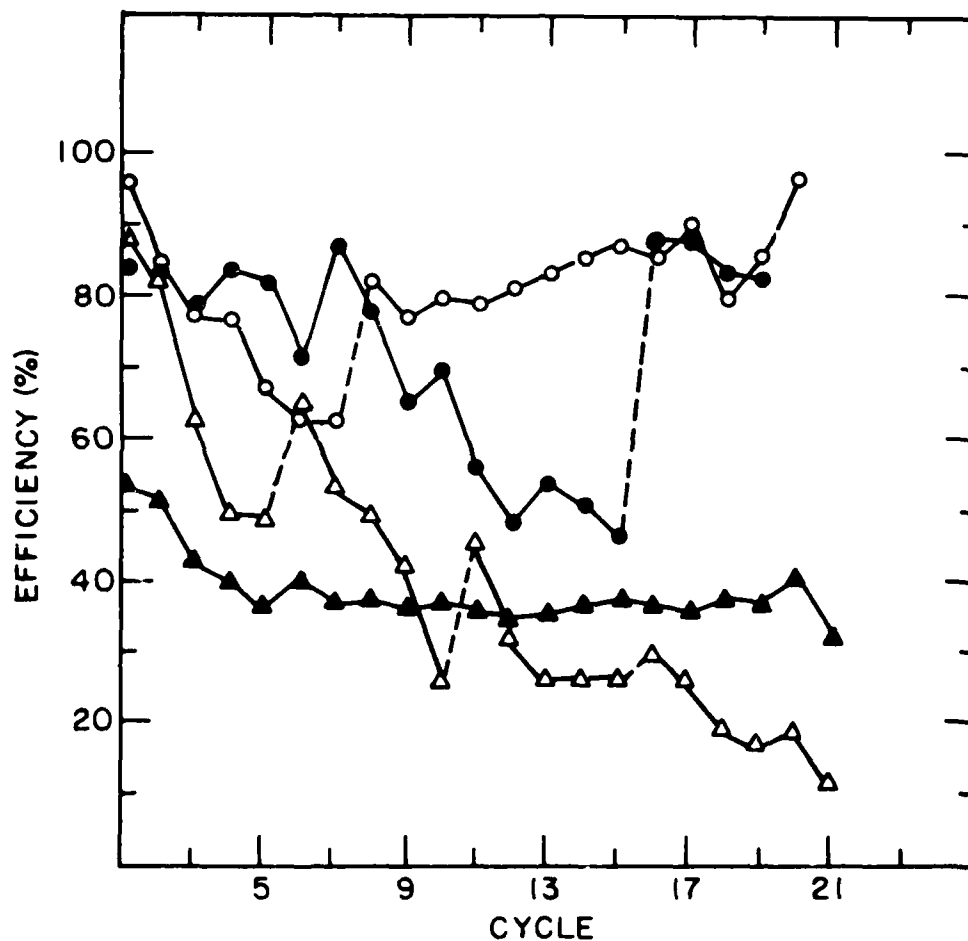


Fig. 8: Repeated cycling of lithium on nickel in propylene carbonate, 1M LiClO₄ with and without SO₂. (○) 1M SO₂, $i_p = i_s = 5 \text{ mA/cm}^2$, $Q_p = 0.33 \text{ coul/cm}^2$, (---) wait 1000 sec; (●) 0.65M SO₂, $i_p = i_s = 10 \text{ mA/cm}^2$, $Q_p = 1 \text{ coul/cm}^2$, with 1000 sec wait between cycles except (---) wait 24 hours; (Δ) 0.65M SO₂, $i_p = i_s = 10 \text{ mA/cm}^2$, $Q_p = 1 \text{ coul/cm}^2$, (---) wait 1000 sec between cycles; (▲) no SO₂, ca. 10 ppm H₂O, $i_p = i_s = 10 \text{ mA/cm}^2$, $Q_p = 1 \text{ coul/cm}^2$.

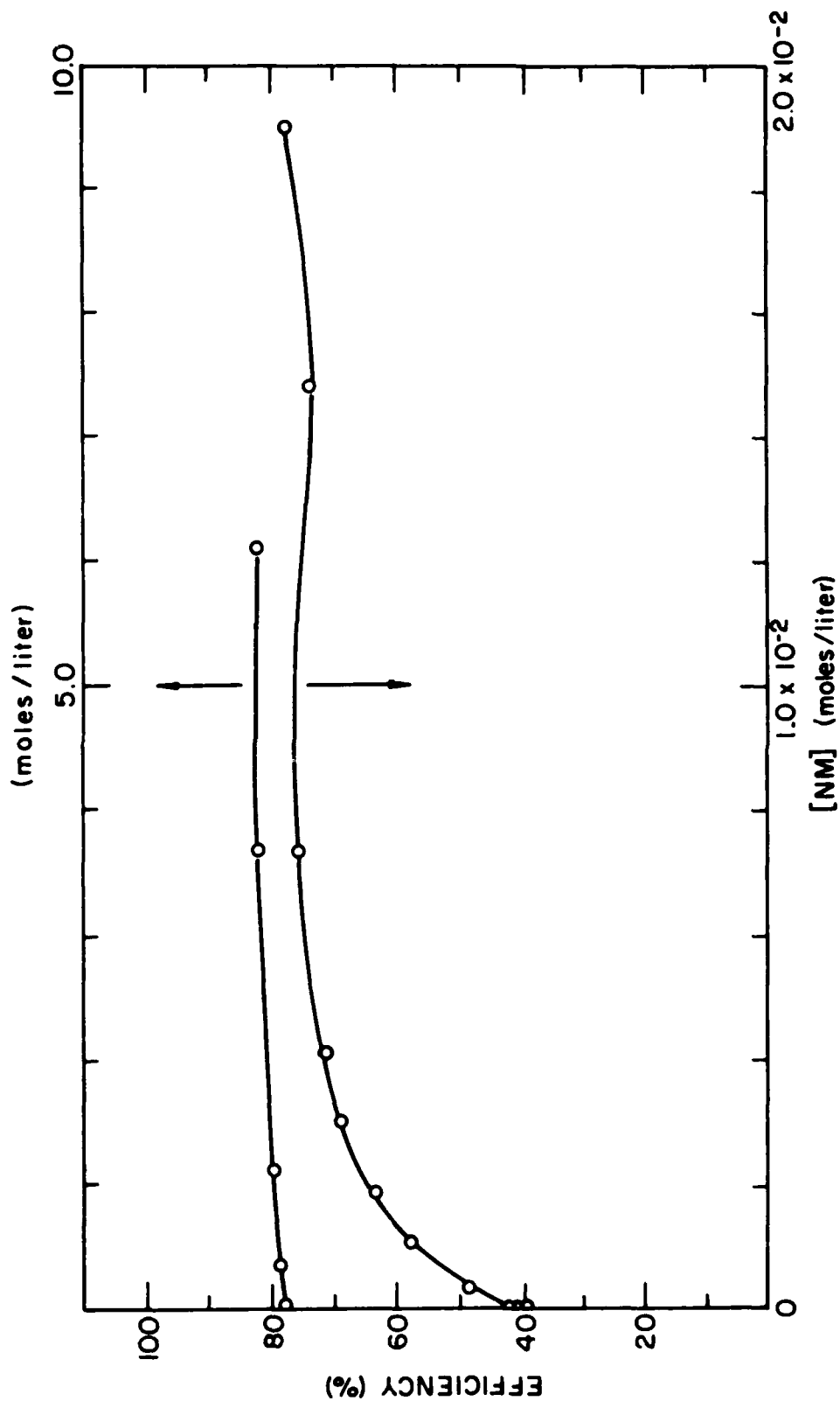


Fig. 9: Efficiency of cycling lithium on a nickel substrate in propylene carbonate, 1M LiClO₄ as a function of concentration of added nitromethane; $i_p = i_s = 10 \text{ mA/cm}^2$; $Q_p = 1 \text{ coul/cm}^2$.

In this solvent, the major effect of SO_2 is upon the efficiency, and not the corrosion current. At the limiting final rate of $5 \mu\text{A}/\text{cm}^2$, a loss of about $0.5 \text{ coul}/\text{cm}^2\text{-day}$ would be expected for electroplated lithium, independent of added SO_2 . A similar experiment substituting LiAlCl_4 for LiClO_4 gave the same high corrosion rate with SO_2 as without, within experimental error (Table 2 and Fig. 6).

Fig. 3 shows the chronopotentiogram for stripping lithium which had been allowed to stand in contact with the PC, 1% SO_2 electrolyte for 1.5 hours. Here, stripping takes place at a higher potential and with a more anodic slope than if it were commenced immediately after plating. This behavior indicates the formation of a resistive film on the deposit in the course of the long term corrosion process. However, it is apparent that if SO_2 reacts with lithium to form a passivating film, the film is ineffective in protecting the electrodeposit from this long term slow attack by the electrolyte. Conceivably water or an acidic species, even in low concentrations, are responsible for much of the corrosion, as they are small enough molecules or ions to penetrate these passivating films. From diffusion theory, a concentration of the order of 5 ppm corrosive species (e.g., H_2O) could account for corrosion currents of $10 \mu\text{A}/\text{cm}^2$.

Nitromethane. Nitromethane (NM), like H_2O and SO_2 , increases the efficiency of lithium cycling, even at low concentrations. A concentration of 10^{-3}M NM was sufficient to raise the efficiency of cycling lithium on a clean nickel surface from 42 to 58%. Higher concentrations of NM caused further increases in efficiency, as reported in Fig. 9.

The results of repeated cycling of NM/PC solutions are shown in Fig. 10. Deterioration of efficiency of cycling a $1 \text{ coul}/\text{cm}^2$ charge begins at the eighth cycle for 0.1M NM solutions, and at approximately the fifteenth cycle for 3.7M NM solutions. Thereafter, the 0.1M solution showed a steeper drop of efficiency with cycle than the 3.7M solution. If significant time were allowed to elapse between cycles, some retardation of the efficiency decline was obtained for these solutions. However, this spiking effect was not nearly as marked as for SO_2 .

Although the cycling efficiency could be improved by adding NM, the corrosion current was the same as for pure PC ($35 \mu\text{A}/\text{cm}^2$ over 8,000 seconds, for $1.5 \text{ coul}/\text{cm}^2$ plated), if the NM were treated for 24 hours over lithium dispersion before use. Initial studies, using untreated spectroquality NM, gave a corrosion rate of $112 \mu\text{A}/\text{cm}^2$ for a 0.1M solution over the same time period. These results are plotted in Fig. 11.

Similar to the case of SO_2 , partially corroded lithium deposits in NM-containing electrolytes show more anodic stripping potentials

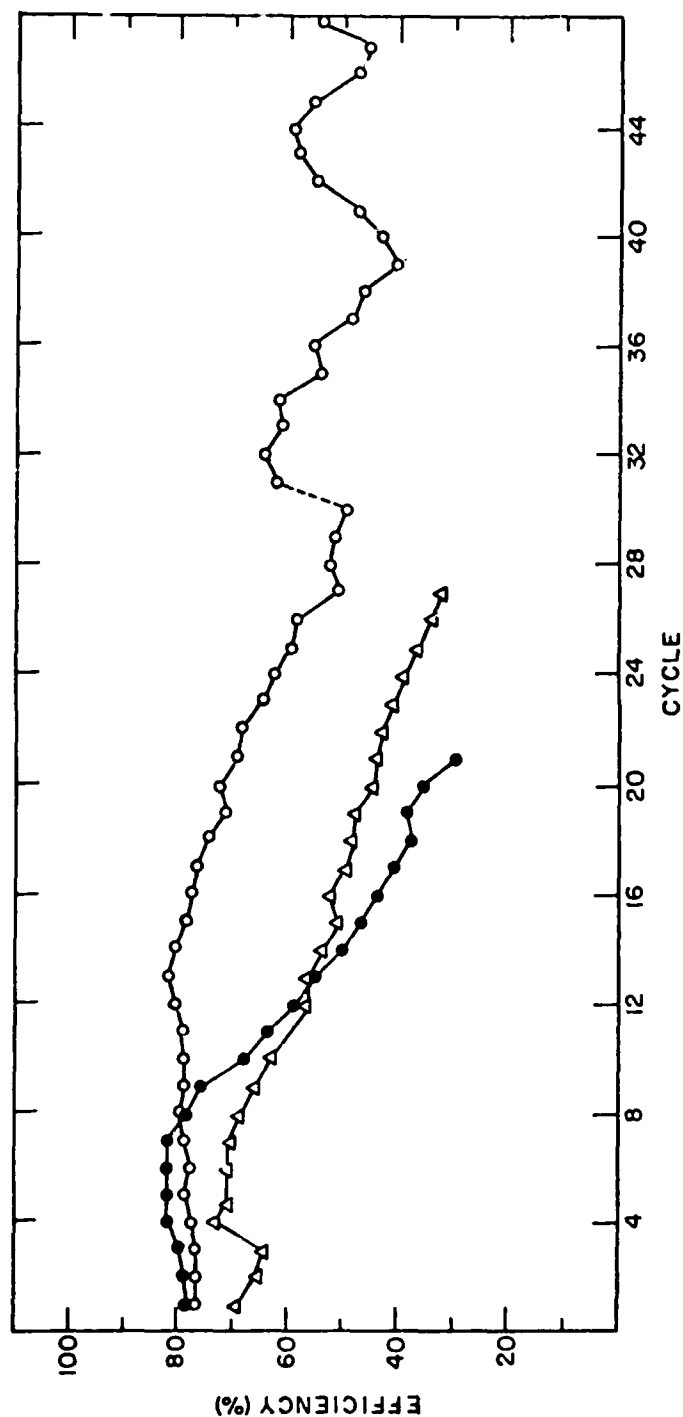


Fig. 10: Repeated cycling of lithium on nickel in propylene carbonate, 1M LiClO₄; $i_p = i_s = 10 \text{ mA/cm}^2$, $Q_p = 1 \text{ coul/cm}^2$; (●) 0.1M nitromethane; (O) 3.7M nitromethane; (Δ) approximately 70 ppm H₂O.

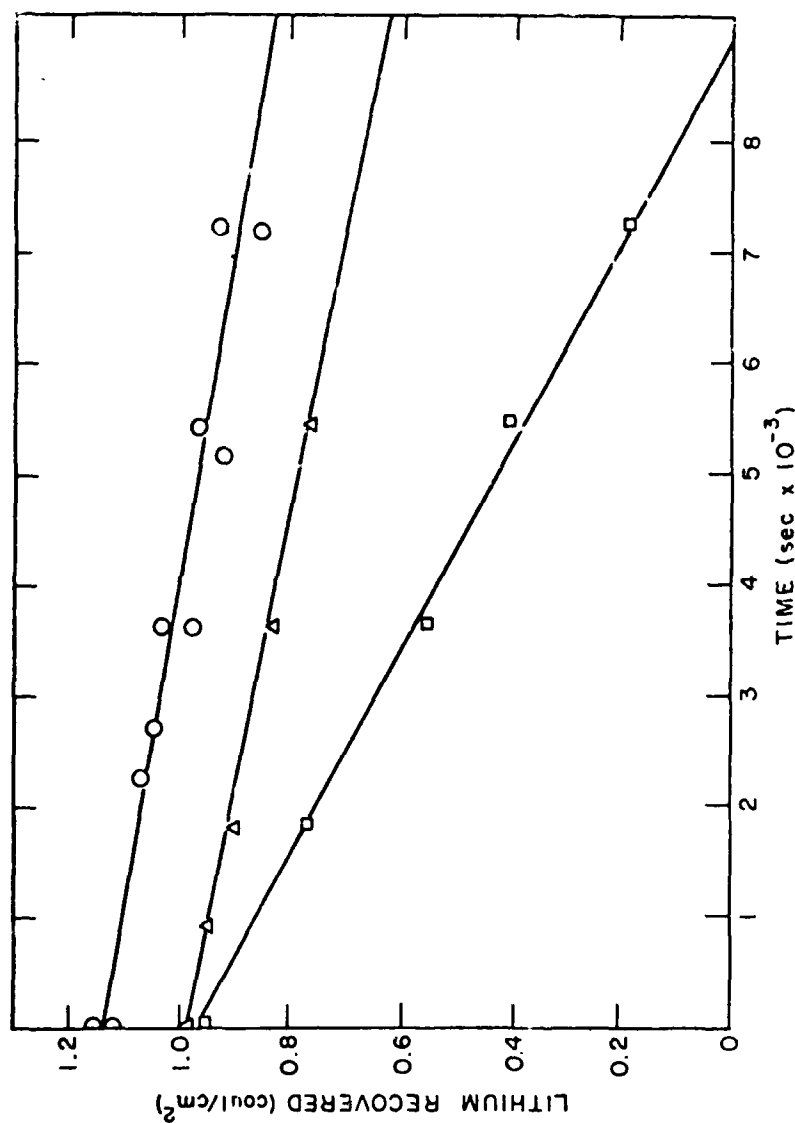


Fig. 11: The short-term corrosion of lithium electrodeposited onto nickel in propylene carbonate, 1M LiClO₄; $i_p = i_s = 5 \text{ mA/cm}^2$; $Q_p = 2 \text{ coul/cm}^2$; (□) 0.1M nitromethane, untreated (O) 0.1M nitromethane pretreated with lithium dispersion; (Δ) no additives.

than deposits removed immediately after plating. As the chronopotentiogram in Fig. 12 indicates, the stripping curve after partial corrosion has a small anodic overshoot, not noted in the case of SO_2 . Such behavior indicates the presence of a resistive film, as with SO_2 , but in this case the film is (partially) destroyed during the stripping cycle.

DISCUSSION

The relative inefficiency of cycling lithium on an inert substrate in PC containing less than 10 ppm H_2O appears due to insulation of the deposit as a result of its reaction with the solvent, or with solvent impurities. This phenomenon has been well documented by Selim and Bro (3), who noted that the true corrosion of lithium deposited in PC on brass, as determined by chemical analysis, was much slower than that observed electrochemically: true corrosion = $0.7 \mu\text{A}/\text{cm}^2$; electrochemical corrosion = $10 \mu\text{A}/\text{cm}^2$.

Microscopic examination shows that corrosion reactions of lithium in PC ultimately destroy the homogeneity of the substrate, which results in an effective decrease in the plating surface area. As the deposit becomes more dendritic with each successive cycle, it appears that all the lithium is plating out in a few small areas on the corrosion-product-covered surface. Hence, the cycling efficiency decreases rather rapidly with cycle number.

In order to formulate a detailed mechanism of the electrochemical loss of deposited lithium, the following experimental results must be taken into account:

1. The dipolar additives studied in this work - H_2O , SO_2 and NM - increase the overall efficiency of lithium cycling in PC. This effect is noticeable even at low concentration of these additives.
2. The initial loss of efficiency coincides with negligible loss of lithium from the electrode, as determined by chemical analysis (3), and is a result of encapsulation and insulation of 20 to 30% of the electrodeposit. This "short term" process is very rapid, and evidently occurs during electroplating.
3. A slower "long term" corrosion process takes place at open circuit stand, which results in further insulation at an initial rate of $43 \mu\text{A}/\text{cm}^2$ in the present system. Evidently, the "true" corrosion rate of the plated lithium, as measured by Selim and Bro (3) by chemical analysis, is less than $1 \mu\text{A}/\text{cm}^2$ in PC, 1M LiClO_4 .
4. Within experimental error, the "long term" corrosion rate of electrodeposited lithium in PC/1M LiClO_4 is little changed by the addition of NM, SO_2 or H_2O (<1200 ppm) (Table 2).

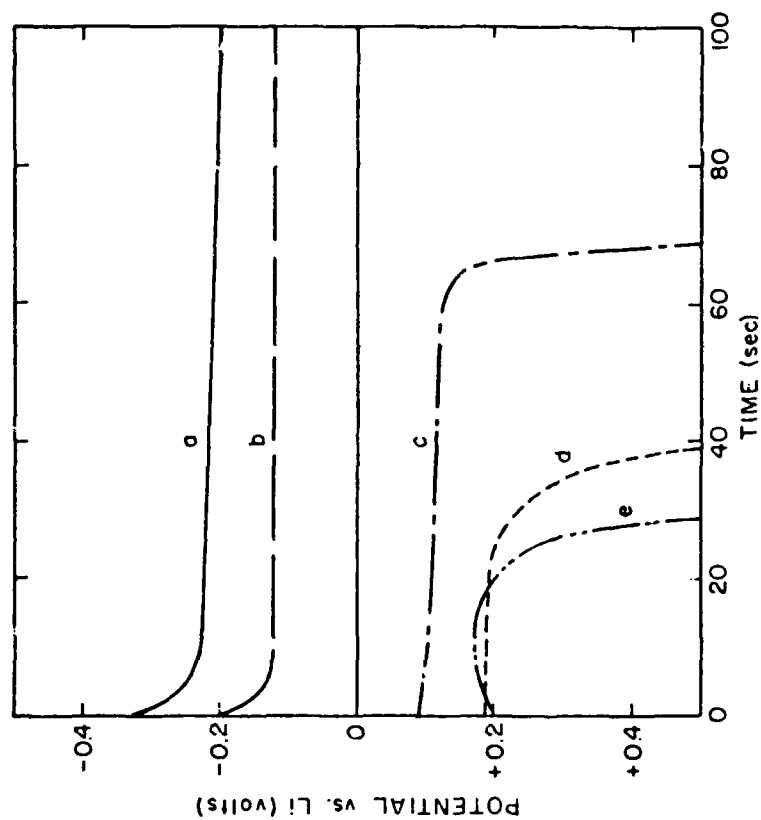


Fig. 12: Lithium plating and stripping chronopotentiograms, on a nickel substrate in propylene carbonate, 1M LiClO₄. $i_p = i_s = 10 \text{ mA/cm}^2$. (a,d) no additives; (b,c) 40% nitromethane added; (e) solution containing 40% nitromethane, with a 10,000 sec wait before stripping.

5. Both the "long term" and "true" (3) corrosion rates decrease with time. However, total passivation ($i_c = 0$) was not observed for this system.

6. The plateau plating and stripping potentials are flatter in the presence of relatively high additive concentrations, as can be seen from Figs. 3 and 10. Without additive (Fig. 3), the plating and stripping curves are likely to show an anodic slope with time.

7. No anodic overshoots were noted on stripping in PC/1M LiClO₄, even after a substantial open circuit stand. At relatively high SO₂ or NM concentrations, the plateau stripping potentials increased by about 100 mV if the deposit were allowed to corrode partially (Figs. 3 and 10). In NM, an anodic overshoot can be detected upon stripping such deposits (Fig. 10).

From these results, it is evident that as-plated lithium is isolated from the substrate through reaction with solvent species. This isolation, however, results in little actual loss of lithium, but rather is the effect of a coating or reaction products on granules of the metal. Such reaction with the electrolyte appears fastest during nucleation and initial deposit growth phases. This "short term" corrosion process is the major reason for the overall inefficiency in cycling lithium. It is partially suppressed by additives. Visual comparison of lithium deposits grown in the presence and absence of additives reveals greater coherence in the former case. The flatter plating and stripping chronopotentiograms obtained in the presence of additives also indicate a more homogeneous deposit.

It is consistent with these results that the additives partially suppress the reaction leading to encapsulation of lithium with insulating products. It is known that polar additives can act as a surface adsorbent on the plating substrate, leading to a more homogeneous plating surface, and thus a smoother deposit (18). Surface adsorbents can also lower the reactivity of the substrate to solvent reduction, thus preventing somewhat the development of resistive areas on the substrate surface due to the products. This would also result in a smoother morphology. However, substrate effects cannot entirely account for the termination of growth, and isolation of lithium granules during plating, or for the low efficiency of cycling small amounts of lithium, in the absence of additives. For example, Selim and Bro's (3) long term corrosion rate, $\sim 10 \mu\text{A}/\text{cm}^2$, was similar to ours, although they use much thicker deposits and a different substrate. The passivation of lithium by SO₂, to form a Li⁺-conductive film, is well known (8), and it is reasonable to postulate that the additives form Li⁺-conductive films on the metal during electrodeposition. Such films, if they rejected PC from the local environment, would permit

the growth of larger lithium granules through retardation of the reaction with the solvent which leads to encapsulation.

The similarity of the "long term" corrosion rates for solutions with and without additives indicates a finite rate of displacement of the conductive additive-induced film by the insulating, and by inference insoluble, electrolyte-induced film. The stripping chronopotentiograms of partially corroded deposits do show the buildup of films in the presence of relatively high concentrations of additives. However, these films seem as ineffective in long-term protection of the deposit as the accumulated lithium-solvent reacting reaction products. The observed reduction of i_c with time is independent of additive, and probably represents both this buildup of reaction products, which limits the rate of diffusion into the interior of the deposit, as well as the greater adherence of some portions of the deposit than others.

It may thus be concluded that for the PC system described, evidence is found for the formation of additive-induced passivating films on open circuit stand, but these films are not effective in totally preventing corrosion of the lithium deposit by the solution. Lithium which is strippable after partial corrosion is covered with the additive-based film, as stripping chronopotentiograms have shown. Partial solubility of these conductive films allows their permeation by solvent molecules, ultimately giving rise to reaction of lithium with the solvent. If the interaction between the conductive film and the solvent were of a more phobic nature, total passivation of the deposit would have a greater chance of occurring.

It was pointed out by Selim and Bro (3) that solvents with a high dielectric constant have some reducible center of positive charge, and hence would be expected to react with lithium. This is especially true of the freshly nucleated material. Hence, solvents for ambient temperature, secondary lithium batteries should be sought which form either Li^+ -conductive, passivating films on the metal, or which, in combination with certain additives, favor the establishment of a Li^+ -conductive truly passivating film. PC, even though unreactive toward lithium on a massive scale, fulfills neither of these criteria.

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